



PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Production of Graft Polymers

We, STERLING MOULDING MATERIALS LIMITED, a British Company, of 8 Heddon Street, London, W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of graft polymers and more especially to the production of toughened polystyrene and styrene copolymers in which a substantially linear polymerised diene hydrocarbon forms the substrate.

Graft polymers are obtained by the polymerisation of one or more olefinic monomers in the presence of a polymer substrate. The production of graft polymers may be used either to modify the properties of the substrate or to modify the properties of the polymer obtainable from the polymerising monomer or monomers.

There have recently come into prominence polymers of diene hydrocarbons which are essentially linear in structure, the greater part of the polymer molecules having been formed by 1,4-addition. In general, such polymers have properties which differ substantially from the polymers obtained by the emulsion polymerisation of the same monomer or monomers in the presence of a free radical-liberating catalyst. The said linear polymers of diene hydrocarbons can be prepared in the presence of several different kinds of catalysts.

It has now been found that polymers of diene hydrocarbons which are substantially linear but amorphous in nature can be used to impart greater impact strength to styrene polymers and at the same time secure a better surface finish on moulded goods prepared therefrom than has hitherto been obtainable with moulded goods produced from the so-called toughened styrene polymers.

According to the present invention there is

provided a process for the production of a graft polymer which comprises heating a solution of a substantially linear, amorphous, rubbery polymer of a conjugated acyclic diene hydrocarbon, having a cis isomer content of at least 30%, in one or more monovinylidene monocyclic aromatic hydrocarbon monomers, with or without a copolymerisable acyclic vinyl monomer, until at least 10% of the monomer or monomers has undergone polymerisation, simultaneously or successively adding to the resulting partially polymerised mixture a plurality of peroxygen polymerisation catalysts which have substantially different decomposition temperatures when heated in the system and gradually raising the temperature of the polymerising mixture.

The preferred rubbery polymers for use in the process of this invention are polybutadiene, polyisoprene and butadiene-isoprene copolymers which are substantially linear and amorphous in nature and contain at least 30% of cis isomer. The cis isomer content may indeed be much greater than this: it may be as high as 90% and even higher. The preferred rubbery polymer is one in which there is over 90% of 1,4 addition of which 32-35% is of the cis configuration.

The monovinylidene monocyclic aromatic hydrocarbon is preferably styrene but other such hydrocarbons, e.g. the vinyl toluenes and the vinyl ethylbenzenes may be used alone or in admixture with each other or with styrene. The copolymerisable acyclic vinyl monomer is preferably acrylonitrile. It is intended that the ultimate polymer should contain a major proportion by weight of units derived from the monovinylidene aromatic hydrocarbon or hydrocarbons and any acyclic vinyl monomer and such materials therefore preferably comprise at least 75% by weight of the solution of rubbery polymer. Preferably such rubbery polymer is present in an amount of 2-20%, even more preferably from 5-12%, of the total weight of the solu-

tion.

In accordance with the process of this invention polymerisation may be initiated in the said solution of rubbery polymer by the action of heat alone or by means of a peroxygen catalyst which initiates substantial polymerisation below 80°C. Polymerisation of the solution is carried on at the minimum temperature at which substantial polymerisation will occur, for example, at about 85-90°C. or, where a catalyst is used, at about 55-60°C. until at least 10% of the monomer or monomers present has or have undergone polymerisation. Stirring of the solution is kept to a minimum during this part of the polymerisation and should be limited to such agitation as is necessary to maintain any precipitated particles of rubbery polymer in suspension and to maintain proper heat transfer through the solution. At this stage one or more peroxygen polymerisation catalysts are dissolved in the polymerising mass. One of these peroxygen catalysts should be of such a nature that it decomposes to initiate substantial polymerisation at a temperature between 80 and 100°C. Further peroxygen catalysts may, if desired, be introduced into the polymerising mass at the same time or, alternatively, they may be added somewhat later. The peroxygen catalysts which initiate substantial polymerisation between 80 and 100°C. include tertiary-butyl hydroperoxide, tertiary butyl peracetate and benzoyl peroxide. The amount of such catalyst is preferably from 0.01-0.10% by weight based upon the weight of the reaction mixture. The temperature of the heated mass is maintained as low as possible consistent with a substantial rate of polymerisation of the monomer or monomers present and may conveniently be between 90-100°C. at this stage. At such temperatures and in the presence of the indicated catalysts approximately 4% per hour of the monomer or monomers will be consumed. Some cooling of the reaction mixture may be necessary to prevent the reaction running away.

When the rate of reaction starts to fall off, the temperature may be gradually raised. If not already present, one or more peroxygen catalysts which initiate substantial polymerisation at temperatures in excess of 100°C. should be introduced. It is much preferred to introduce two such catalysts at this juncture; one of these should initiate substantial polymerisation at a temperature at least 10°C., preferably 20°C., lower than the temperature at which the other does so. The temperature is then raised until a temperature is reached at which one of these catalysts is effective in initiating polymerisation and, when the polymerisation initiating tendency of this catalyst starts to fall off, the temperature is again raised until a temperature is reached at which the other of these cata-

lysts is effective. The first of these two catalysts preferably undergoes substantial decomposition in the polymerising system at temperatures of 105-125°C. and the second at 125°-150°C. Examples of catalysts lying within the first group are cumene hydroperoxide and tertiary-butyl perbenzoate and examples lying within the second group are dicumyl peroxide and ditertiarybutyl peroxide. Catalysts of the first group are preferably present in amounts of 0.01-0.10% by weight, based upon the weight of the reaction mixture, whilst catalysts within the second group are preferably present in amounts of 0.03-0.10%, upon the same basis. The polymerisation is completed by gradually raising the temperature of the polymerising mass to about 180°C., at which temperature the mass may be held for several hours in order to carry polymerisation to substantial completion.

Whilst it has been indicated that the different peroxygen catalysts may be added separately it is much preferred to add all of the catalysts at one time since the viscosity of the polymerising mixture at the time when the initial monomeric solvent has polymerised to the extent of about 10 to 25% is comparatively low and it is therefore relatively easy to secure a substantially uniform dispersion of the catalysts throughout the reaction mixture at this stage. The presence of those catalysts which initiate polymerisation at the higher temperatures indicated does not interfere with the action of the catalysts which are effective at the lower temperatures.

According to a feature of the invention, the reaction mixture also contains a chain transfer agent such as *n*-lauroyl mercaptan; this reduces the average molecular weight of the resulting polymer.

Other conventional additives such as a mould lubricant may also be included in the polymerising mixture.

The products of the invention are suitable for use at low temperatures since they possess as good or better impact strength than the so-called toughened polystyrene produced from a substrate of a conventionally prepared butadiene-styrene copolymer. The impact strength at room temperature is also generally higher. In addition the appearance of moulded articles produced from the products of the present invention is markedly superior to that of comparable materials hitherto available.

The following Examples illustrate the nature of the invention and the manner in which it may be carried into effect, the percentages being calculated by weight.

EXAMPLE I

The reaction is carried out in a stainless steel reactor, provided with a stirrer and a condenser. The polybutadiene polymer sold

under the trade name "Diene" (a substantially linear polymer of butadiene having over 90% of 1,4-addition product and 7.5% of vinyl structure) was dissolved in styrene by stirring for 5 hours at 60°C. to the extent necessary to form a 6% solution. The temperature of the rubber solution is raised to 85°C-90°C. and it is polymerised until 12% of the styrene has been polymerised. The following initiators are then added simultaneously: tertiary-butyl hydroperoxide 0.02%, cumene hydroperoxide 0.02% and di-cumyl peroxide 0.05% and 0.05% of *n*-lauroyl mercaptan, together with 1% of butyl stearate, all amounts being based on the weight of the total solution. The resulting mass is reacted until the total solids content is 40%. The stirrer was removed at this stage and the temperature of the mass allowed to rise slowly

above 100°C. As the thermal reaction and the catalytic reaction are both taking place at this stage the reaction is relatively fast and is usually completed within four hours. Cooling had to be applied to the reactor to keep the temperature under control. Finally the reactor is heated at 130°C. for 3 hours, at 150°C. for 2 hours and finally at 180°C. for 3 hours.

The block of polymer thus obtained is ground, extruded and test pieces are moulded on a 2.25 oz. Hupfield Injection Moulding machine. The Table below gives the results obtained for impact strength measurement at low temperatures when compared with conventional toughened polystyrene made by polymerising styrene monomer in which is dissolved a rubbery butadiene-styrene copolymer.

Material	Impact Strength		
	23°C.	-25°C.	-50°C.
Prepared as in Example I	1.8	1.4	1.3
Conventional Material	1.2	0.8	0.6
	1.5	1.3	0.4

The impact tests have been carried out using $\frac{1}{4}$ " \times $\frac{1}{2}$ " notched bars according to British Standards Specification No. 3126.

EXAMPLE II

A solution of polybutadiene rubber in styrene is prepared as in Example I. The temperature of the rubber solution is raised to 90°C. with stirring and the speed of the stirrer, anchor type, is adjusted to 32 R.P.M. The solution is heated until 12% of the styrene has been polymerised. Then the following initiators are added: tertiary-butyl hydroperoxide 0.02%, cumene hydroperoxide 0.02% and di-cumyl peroxide 0.05% and 0.05% of *n*-lauroyl mercaptan, together with 1% of butyl stearate. Then the mass is allowed to react until the total solids content is 40%. The stirrer is removed at this stage and the temperature of the mass is allowed to rise above 100°C. Cooling is applied to prevent a runaway reaction.

Finally the reactor is heated to 130°C. for 3 hours, to 150°C. for 2 hours and then for 3 hours at 180°C. The material is moulded as described in Example I and the impact strength determined as in Example I.

Impact strength at 23°C. was found to be 2.1 ft.lb./inch notch.

If the stirrer speed is too high there is

a reduction in the impact strength as may be seen from the fact that in this example a stirrer speed of 64 R.P.M. would result in a product having an impact strength of 1.2 ft.lb./inch notch.

EXAMPLE III

A graft polymer is prepared using the same method of preparation as in Example II except that the rubber used is a linear polybutadiene having a cis content of 92% and is sold under the name Polysar XPRD A 335 (the word "Polysar" is a Registered Trade Mark).

Mouldings were prepared and their impact strength determined as described in Example I.

Impact strength at 23°C. was found to be 1.9 ft.lb./inch notch.

The mouldings possess an excellent gloss which is far superior to that of conventional toughened polystyrene.

EXAMPLE IV

"Diene" rubber is dissolved in vinyl toluene by stirring for 5 hours at 60°C. to form a 6% solution. The temperature of the rubber solution is raised to 85°C. and it is polymerised until about 12% of the vinyl toluene has polymerised. The addition of

the initiators and the remainder of the preparation was carried out as in Example II.

Mouldings were prepared and their impact strength determined as in Example I was found to be 1.8 ft.lb./inch notch.

EXAMPLE V

"Diene" rubber is dissolved in a monomer mixture consisting of styrene and acrylonitrile at 50°C. for 6 hours to form a solution containing 15% Diene, 55% of styrene and 30% of acrylonitrile.

Then 0.05% of diisopropylpercarbonate is added, the stirrer speed adjusted to 32 R.P.M. and the temperature raised to 55°C. until the total solids content is 25%.

0.02% of tertiary-butyl peroxide, 0.02% of ditertiary-butyl peroxide, 0.02% of dicumyl peroxide and 0.05% of dodecyl mercaptan are added and the temperature is raised to 80°C. The mixture is polymerised to 33% total solids, at which point the stirrer is removed from the reacting mass and the temperature is allowed to rise slowly, within 8 hours, to 160°C. Then the reactor is heated for 1 hour at 120°C., 1 hour at 130°C., 2 hours at 150°C. and 2 hours at 180°C.

Mouldings were prepared and their impact strength determined as in Example I which was found to be 3.6 ft.lb./inch notch.

Various modifications may be made in the method of preparation of the polymers as illustrated in the foregoing Examples. The reaction may, for example, be completed in a second reactor to avoid removing the stirrer from the mass after 40% of the monomer has polymerised. In this modification the reacting mass is discharged just before the total solids reach 40% into a reactor provided with coils, through which water or steam can be circulated and with frames and platens in which the final product is shaped. The temperature of the subdivided mass in the frames is allowed to rise to 160-180°C., as a result of the exothermic reaction, within 6 to 8 hours. Then the second reactor is heated to 120°C. for 1 hour, 130°C. for 1 hour, 140°C. for 1 hour and 2 hours at 180°C.

It will be appreciated that, as is conventional in polymerisation processes, any residual monomeric material is removed from the reaction mixture by distillation, if necessary, under reduced pressure, if required.

WHAT WE CLAIM IS:—

1. A process for the production of a graft polymer which comprises heating a solution of a substantially linear, amorphous, rubbery polymer of a conjugated acyclic diene hydrocarbon, having a cis isomer content of at least 30%, in one or more monovinylidene mono-

cyclic aromatic hydrocarbon monomers, with or without a copolymerisable acyclic vinyl monomer, until at least 10% of the monomer or monomers has undergone polymerisation, simultaneously or successively adding to the resulting partially polymerised mixture a plurality of peroxygen polymerisation catalysts which have substantially different decomposition temperatures when heated in the system and gradually raising the temperature of the polymerising mixture.

2. A process according to claim 1 wherein the rubbery polymer is present in an amount of from 2 to 20% by weight of the solution.

3. A process according to claim 1 wherein the rubbery polymer is present in an amount of from 5 to 12% by weight of the solution.

4. A process according to any of the preceding claims wherein one or more of the peroxygen polymerisation catalysts initiate substantial polymerisation at a temperature below 100°C. and the remaining catalyst or catalysts initiate substantial polymerisation at a temperature above 100°C.

5. A process according to claim 4 wherein two catalysts which initiate substantial polymerisation at a temperature above 100°C. are employed and one of these two catalysts initiates substantial polymerisation at a temperature from 10° to 20°C. below the temperature at which the other initiates such polymerisation.

6. A process according to any of the preceding claims wherein a peroxygen polymerisation catalyst which initiates substantial polymerisation below a temperature of 80°C. is added to the solution of the rubbery polymer prior to the commencement of the polymerisation reaction.

7. A process according to any of the preceding claims wherein the reaction mixture contains a chain transfer agent.

8. A process according to any of the preceding claims wherein agitation of the said solution is limited to what is necessary to maintain any precipitated particles of rubbery polymer in suspension until at least 10% by weight of the monomeric material has undergone polymerisation.

9. A process according to any of the preceding claims wherein the vinylidene aromatic hydrocarbon is styrene.

10. A process according to any of the preceding claims wherein said copolymerisable acyclic vinyl monomer is acrylonitrile.

11. A process for the production of a graft polymer substantially as described with reference to any of the Examples.

12. Graft polymers when produced by the process claimed in any of the preceding claims.

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and
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